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(54) [Title of the Invention] Optical Recording Medium

(57) [Abstract]

[Means for Solution] An optical recording medium comprised of a substrate 1 on which at least a recording layer 2 and a light reflecting layer 3 are formed, said optical recording medium characterized in that said light reflecting layer is mainly comprised of silver and has an average crystal particle size of 200 to 600Å.

[Effects] According to the present invention, it is possible to provide a light recording medium having excellent recording and reproducing characteristics and excellent in durability.

## [CLAIMS]

[Claim 1] An optical recording medium comprised of a substrate on which at least a recording layer and a light reflecting layer are formed, said optical recording medium characterized in that said light reflecting layer is mainly comprised of silver and has an average crystal particle size of 200 to 600Å.

[Claim 2] An optical recording medium as set forth in claim 1, wherein the recording layer consists of a phthalocyanine dye.

[Claim 3] An optical recording medium as set forth in claim 1 or 2, wherein the substrate is provided with a recording layer, a light reflecting layer, and a protective layer in that order.

## [DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field of the Invention] The present invention relates to an optical recording medium, more particularly an optical recording medium which has a light reflecting layer.

[0002]

[Prior Art] In recent years, write-once or recordable compact disks (CD) (CD-R) meeting the specifications of compact disks have been proposed as optical recording media comprised of substrates having light reflecting layers (for example, *Nikkei Electronics* No. 465, p. 107, January 23, 1989 issue). This optical recording medium, as shown in FIG. 1, is comprised of a substrate 1 on which a recording layer 2, a light reflecting layer 3, and a protective layer 4 are formed in that order. The recording layer of the optical recording medium is irradiated by a semiconductor laser or other laser light at a high power. Therefore, the recording layer undergoes a physical or chemical change and information is recorded in the form of pits. By irradiating low power laser light to the formed pits and detecting the reflected light, the information

of the pits can be reproduced.

[0003] On the other hand, compact disks, laser disks, and other read only optical recording media being used instead of music records have the music information recorded beforehand on the surface of the substrates in the form of pits and are structured as substrates on which Al or Au or other light reflecting layers and protective layers for protecting the same are formed. This is basically the same structure as a write-once or recordable CD except for the provision of the recording layer instead of the bit part of the substrate surface. A CD-R finished being recorded on can be played back by an ordinary CD player in the same way as a read only CD.

[0004]

[Problem(s) to be Solved by the Invention] The CD-Rs currently marketed are produced by successively providing a transparent substrate with a recording layer comprised of an organic dye, a light reflecting layer comprised of a metal, and a protective layer comprised of a UV curing resin in that order. As the light reflecting layer, since there is the recording layer with absorption at the wavelength of the laser light, normally the high reflectivity Au is used as the light reflecting layer. Gold, however, is expensive, so this is becoming a problem in terms of costs. On the other hand, when using silver, copper, or another metal which is inexpensive compared with gold, but has high reflectivity on a par with gold or alloys mainly comprised of the same as the light reflecting layer, a drop in reflectivity due to corrosion of the light reflecting layer or a change in the disk characteristics such as the error rate easily occur, so it was difficult to produce durable CD-Rs.

[0005]

[Means for Solving the Problem] The present invention has as its object to solve the above problems in the prior art and provide a low cost CD-R by maintaining durability equivalent

to that of a CD-R using high corrosion resistance gold as a light reflecting layer and using a reflective layer comprised mainly of a cheaper metal, in particular silver, as the light reflecting layer.

[0006] The present inventors engaged in intensive studies to solve the above problem and as a result propose the present invention. That is, the problem is solved by the following aspects of the invention:

(1) An optical recording medium comprised of a substrate on which at least a recording layer and a light reflecting layer are formed, said optical recording medium characterized in that said light reflecting layer is mainly comprised of silver and has an average crystal particle size of 200 to 600Å, (2) an optical recording medium as set forth in (1), wherein the recording layer consists of a phthalocyanine dye, and (3) an optical recording medium as set forth in (1) or (2), wherein the substrate is provided with a recording layer, a light reflecting layer, and a protective layer in that order.

[0007]

[Embodiments of the Invention] The concrete configuration of the present invention is explained below. The optical recording medium of the present invention has a light reflecting layer on a substrate. The "optical recording medium" indicates both a read only optical read only medium on which information is recorded in advance and an optical recording medium able to record and reproduce information. Here, however, as a suitable example, the explanation is given with reference to the latter optical recording medium able to record and reproduce information, in particular an optical recording medium comprised of a substrate on which a recording layer, light reflecting layer, and protective layer are formed in that order. This optical recording medium has a four-layer structures as shown in FIG. 1. That is, the substrate 1 is formed with the

recording layer 2, the light reflecting layer 3 is formed in close contact above it, and the protective layer 4 covers the light reflecting layer 3.

[0008] The material of the substrate of the present invention basically need only be transparent to the wavelength of the recording light and reproduction light. For example, a polycarbonate resin, vinyl chloride resin, polymethyl methacrylate or other acrylic resin, polystyrene resin, epoxy resin, or other polymeric material or glass or another inorganic material is used. Such substrate materials are fabricated into disk shaped substrates by injection molding etc. Grooves may be formed in the substrate surface if needed.

[0009] As the recording layer in the present invention, one containing a dye is preferable. More preferably, the dye is a phthalocyanine dye. In particular, a phthalocyanine dye having a substituent, having a metal atom at its center, and able to dissolve in an organic solvent is used. As this substituent, a nonsubstituted alkyl group, aryl group, unsaturated alkyl group, alkoxyl group, aryloxy group, unsaturated alkoxyl group, alkylthio group, arylthio group, unsaturated alkylthio group, carboxyl group, carboxylic-acid amide group, silyl group, amino group, etc. may be mentioned.

[0010] As more concrete examples of the aforementioned substituent, as an alkyl group, a methyl group, ethyl group, n-propyl group, n-butyl, isobutyl group, n-pentyl group, neopentyl group, isoamyl group, 2-methylbutyl, n-hexyl group, 2-methylpentyl group, 3-methylpentyl group, 4-methylpentyl group, 2-ethylbutyl, n-heptyl group, 2-methylhexyl group, 3-methylhexyl group, 4-methylhexyl group, 5-methylhexyl group, 2-ethylhexyl group, 3-ethylpentyl group, n-octyl group, 2-methylheptyl group, 3-methylheptyl group, 4-methylheptyl group, 5-methylheptyl group, 2-ethylhexyl group, 3-ethylhexyl

group, n-nonyl group, n-decyl group, n-dodecyl group, and other primary alkyl groups, an isopropyl group, sec-butyl group, 1-ethylpropyl group, 1-methylbutyl group, 1,2-dimethylpropyl group, 1-methylheptyl group, 1-ethylbutyl group, 1,3-dimethylbutyl group, 1,2-dimethylbutyl group, 1-ethyl-2-methylpropyl group, 1-methylhexyl group, 1-ethylheptyl group, 1-propylbutyl group, 1-isopropyl-2-methylpropyl group, 1-ethyl-2-methylbutyl group, 1-propyl-2-methylpropyl group, 1-methylheptyl group, 1-ethylhexyl group, 1-propylpentyl group, 1-isopropylpentyl group, a 1-isopropyl-2-methylbutyl group, 1-isopropyl-3-methylbutyl group, 1-methyloctyl group, 1-ethylheptyl group, 1-propylhexyl group, 1-isobutyl-3-methylbutyl group, and other secondary alkyl groups, a tert-butyl group, tert-hexyl group, tert-amino group, tert-octyl group, or other tertiary alkyl groups, a cyclohexyl group, 4-methylcyclohexyl group, 4-ethylcyclohexyl group, 4-tert-butylcyclohexyl group, 4-(2-ethylhexyl)cyclohexyl group, bornyl group, isobrunyl group, adamantane group, or other cycloalkyl groups etc.; as an aryl group, a phenyl group, ethylphenyl group, butylphenyl group, nonylphenyl group, naphthyl group, butylnaphthyl group, nonylnaphthyl group, etc.; and as an unsaturated alkyl group, an ethylene group, propylene group, butylene group, hexene group, octene group, dodecene group, cyclohexene group, butylhexene group, etc. may be mentioned.

[0011] Moreover, these alkyl groups, aryl groups, and unsaturated alkyl groups may be substituted by a hydroxyl group, halogen group, etc. or may be substituted by the aforementioned alkyl groups and aryl groups through atoms such as oxygen, sulfur, and nitrogen. As an alkyl group or an aryl group substituted through oxygen, a methoxymethyl group, methoxyethyl group, ethoxymethyl group, ethoxyethyl group,

butoxyethyl group, ethoxyethoxyethyl group, phenoxyethyl group, methoxypropyl group, ethoxypropyl group, methoxyphenyl group, butoxyphenyl group, polyoxyethylene group, polyoxyethylene group, polyoxypropylene group, etc.; as an alkyl group or an aryl group substituted through sulfur, a methylthioethyl group, ethylthioethyl group, ethylthiopropyl group, phenylthioethyl group, methylthiophenyl group, butylthiophenyl group, etc.; and as an alkyl group or an aryl group substituted through nitrogen, a dimethylaminoethyl group, diethylaminoethyl group, diethylaminopropyl group, dimethylaminophenyl group, dibutylaminophenyl group, etc. may be mentioned. On the other hand, as a central metal of a phthalocyanine dye, a divalent metal is desirable. Specifically, Ca, Mg, Zn, Cu, Ni, Pd, Fe, Pb, Co, Pt, Cd, Ru, etc. may be mentioned. Moreover, it may be a metallic oxide such as a vanadyl group (VO).

[0012] Moreover, the above-mentioned phthalocyanine dye may in accordance with need be comprised of two or more types of phthalocyanine dyes mixed together and may include a light absorbent, combustion improver, quencher, UV absorbent, adhesive, resin binder, or other additive mixed in or as a substituent.

[0013] The light absorbent spoken of here has absorption at the wavelength of the recording light and raises the sensitivity of a phthalocyanine dye film. An organic dye is desirable. For example, a naphthalocyanine dye, porphyrin dye, azo dye, pentamethine cyanine dye, squarylium dye, pyrylium dye, thiopyrylium dye, azulanium dye, naphthoquinone dye, anthraquinone dye, indophenol dye, triphenylmethane dye, xanthene dye, indanthrene dye, indigo dye, thioindigo dye, merocyanine dye, thiazine dye, acridine dye, oxazine dye, etc. are often used. Among these, a naphthalocyanine dye is particularly preferable from the standpoint of the absorbed

wavelength area. These dyes may further be used mixed together.

[0014] As examples of a combustion improver, a metal-based anti knocking agent tetraethyl lead, tetramethyl lead, and other lead compounds, cymantrene ( $\text{Mn}_3(\text{C}_5\text{H}_5)(\text{CO})_3$ ) and other Mn compounds, the metallocene compound iron bis(cyclopentadienyl) complex (ferrocene) and Ti, V, Mn, Cr, Co, Ni, Mo, Ru, Rh, Zr, Lu, Ta, W, Os, Ir, Sc, Y, and other bis(cyclopentadienyl) metal complexes can be mentioned. Among these, ferrocene, rutenocene, osmocene, nickelocene, titanocene and their derivatives have a good combustion improving effect. As iron metallic compounds, besides metallocene, iron formate, iron oxalate, iron laurate, iron naphthenate, iron stearate, iron butyrate, and other organic acid iron compounds, acetylacetonate iron complex, phenanthroline iron complex, bipyridine iron complex, ethylenediamine iron complex, ethylenediaminetetraacetic acid iron complex, diethylenetriamine iron complex, diethyleneglycol methyl ether iron complex, diphosphino iron complex, dimethylglyoxylate iron complex, and other chelate iron complexes, a carbonyl iron complex, cyano iron complex, ammine iron complex, or other iron complex, ferric and ferrous chloride, ferric and ferrous bromide, and other halogenated iron or iron nitrate, iron sulfate, and other inorganic iron salts or iron oxide etc. may be mentioned. The iron metallic compounds used here is preferably one which can dissolve in an organic solvent and is excellent in humidity and heat resistance and light resistance. In particular, an acetylacetonato iron complex, iron-carbonyl complex, etc. are extremely preferable in the point of enabling good solubility. If needed, the above-mentioned combustion improver may have a substituent introduced, may be mixed, or may include a binder or other additive.



[0015] These dyes are formed into a film on the substrate by spin coating, casting, sputtering, chemical vapor deposition, vacuum deposition, etc. In the present invention, in order to form the dye film in a specific shape at the pit section and the groove section, spin coating is most suitable.

[0016] In spin coating, a coating solution in which the dye is dissolved or dispersed is used. At this time, the solvent is preferably selected from ones not damaging the substrate. For example, n-hexane, n-octane, isooctane, or another aliphatic hydrocarbon solvent, cyclohexane, methylcyclohexane, ethylcyclohexane, propylcyclohexane, dimethylcyclohexane, diethylcyclohexane, or another cyclic-hydrocarbon solvent, benzene, toluene, xylene, ethylbenzene, or another aromatic hydrocarbon solvent, chloroform, carbon tetrachloride, dichloromethane, 2,2,3,3-tetrafluoro-1-propanol, or another halogenated hydrocarbon solvent, methanol, ethanol, 1-propanol, 2-propanol, diacetone alcohol, or another alcohol solvent, dioxane, tetrahydrofuran, diethyl ether, dibutyl ether, diisopropyl ether, or another ether solvent, methyl cellosolve, ethyl cellosolve, or another cellosolve solvent, acetone, methyl isobutyl ketone, ethyl acetate, or another ketone solvent, ethyl acetate, methyl acetate, butyl acetate, or another ester solvent, etc. may be mentioned. These organic solvents may be used alone or in mixtures of two or more types.

[0017] In formation of a phthalocyanine dye film, among the above-mentioned coating solvents, it is possible to use n-octane, ethylcyclohexane, dimethylcyclohexane, or another organic solvent having a boiling point of about 120 to 140°C alone or one of these plus dioxane, xylene, toluene, propylcyclohexane, etc. mixed in a volume ratio of about 0.1 to 10%.

[0018] As the preferable coating conditions, for example, the dye solution is coated under an environment of a temperature

of  $24^{\circ}\text{C} \pm 1^{\circ}\text{C}$  at an initial low speed (100 to 1000 rpm) for 1 to 10 seconds, then immediately dried under the same environment at a high speed (2000 to 5000 rpm) for 10 to 60 seconds, whereby a uniform dye film can be formed. Moreover, in accordance with need, it is possible to form not just one recording layer, but a plurality of layers of dyes. The thickness of the recording layer is about 10 to 200 nm.

[0019] Next, a light reflecting layer is formed on the recording layer. In the present invention, it is desirable to use a metal film mainly comprised of silver as the light reflecting layer and make the average crystal particle size of the silver 200 to 600Å, preferably 300 to 500Å. The particle size can be measured with a transmission electron microscope (TEM) etc.

[0020] When the crystal particle size of the silver reflecting layer is smaller than 200Å, the reflectivity becomes lower and reproduction sometimes becomes impossible. Moreover, when the crystal particle size is larger than 600Å, when performing an  $80^{\circ}\text{C}$  85%RH humidity and heat resistance test, large numbers of defects occur due to agglomeration of the silver etc. In the worst case, reproduction becomes impossible. As the thickness of the silver reflecting layer, one in the range of 700 to 1500Å, preferably 800 to 1200Å, is preferable.

[0021] As the method of forming the reflecting layer, for example, the methods of forming a thin film by sputtering, chemical vapor deposition, vacuum deposition, ion plating, etc. may be mentioned. Among these, sputtering is the technique used most often. The crystal particle size of the silver reflecting layer can be controlled by suitably setting the amount of addition of impurities in the silver or the above-mentioned film forming conditions.

[0022] As impurities, it is possible to add metals selected from the group comprised of indium, rhodium, palladium, platinum, titanium, molybdenum, tantalum, zirconium, vanadium,

tungsten, copper, zinc, and nickel alone or in mixtures. As the amount added, if too large, the crystal particle size will become smaller, but the reflectivity will end up falling, so about 0.1 to 5atm% is suitable. Note that as the sputter power is made larger or the gas pressure is made lower, there is a tendency for the crystal particle size to become smaller, so it is possible to easily determine the suitable sputter power or gas pressure experimentally.

[0023] Moreover, in order to raise the reflectivity or to improve the adhesion, a reflection amplifying layer, adhesive layer, or other intermediate layer may be provided between the recording layer and reflecting layer. As the material used for the intermediate layer, one having a large refractive index at the wavelength of the reproduction light is desirable. For example, as an inorganic material, there are  $\text{Si}_3\text{N}_4$ ,  $\text{AlN}$ ,  $\text{ZnS}$ , a  $\text{ZnS}$  and  $\text{SiO}_2$  mixture,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{CeO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{ZnSe}$ ,  $\text{Sb}_2\text{S}_3$ , etc. These materials may be used alone or mixed together. On the other hand, as an organic material, a cyanine dye, phthalocyanine dye, naphthalocyanine dye, porphyrin dye, azo dye, squarylium dye, pyrylium dye, thiopyrylium dye, azulanium dye, naphthoquinone dye, anthraquinone dye, indophenol dye, triphenylmethane dye, xanthene dye, indanthrene dye, indigo dye, thioindigo dye, merocyanine dye, thiazine dye, acridine dye, oxazine dye, or other dye or polystyrene, polyvinyl acetate, polycarbonate, polyethylene, polypropylene, polyacrylic ester, polymethacrylic acid ester, styrene-acrylonitrile copolymer, polyvinyl alcohol, polyvinyl acetal, polyvinyl butyral, polyvinyl formal, polyvinyl pyrrolidone, poly p-hydroxystyrene, and other polymeric materials may be mentioned.

[0024] Furthermore, the reflecting layer may have a protective layer formed on it. The material of the protective layer is not particularly limited so long as the layer protects the

reflecting layer from external force. As an organic substance, a thermoplastic resin, thermosetting resin, UV curing resin, etc. can be mentioned. A UV curing resin is desirable. On the other hand, as an inorganic substance,  $\text{SiO}_2$ ,  $\text{SiN}_4$ ,  $\text{MgF}_2$ ,  $\text{SnO}_2$  etc. can be mentioned. Note that it is also possible to form this by dissolving a thermoplastic resin, thermosetting resin, etc. in a suitable solvent, coating the coating solution, and drying it. With a UV curing resin, the layer can be formed by coating the resin as it is or dissolving it in a suitable solvent to prepare a coating solution and coating the coating solution, then irradiating UV light to cure the resin. As the UV curing resin, for example, urethane acrylate, epoxy acrylate, polyester acrylate, or another acrylate resin can be used. These materials may be used alone or mixed together. There is nothing stopping forming not just one layer, but multiple layers.

[0025] As the method of forming the protective layer, in the same way as the recording layer, spin coating, casting, or other coating method or sputtering, chemical vapor deposition, or other method may be used. Among these, spin coating is preferable. The thickness of the protective layer is about 1 to 15  $\mu\text{m}$ .

[0026]

[Mode of Operation] According to the present invention, by controlling the crystal particle size of the silver reflecting layer to a range of 200 to 600Å, an optical recording medium excellent in durability and excellent in recording/reproducing characteristics is provided.

[0027]

[Examples] Below, examples of the present invention will be shown, but the present invention is not limited to these.

[Example 1] 0.25 g of phthalocyanine dye shown in the following formula (1) (Formula 1) was dissolved in 10 ml of a coating

solution comprised of ethylcyclohexane plus 3% o-xylene to prepare a dye solution. The substrate used was a disk made of a polycarbonate resin, having a continuous guide groove, and having a diameter of 120 mm and a thickness of 1.2 mm. The substrate was spin coated with the dye solution by a speed of 1500 rpm and dried at 70°C for 2 hours to form a 100 nm recording layer.

[0028] This recording layer then was formed on it with a silver reflecting layer of a thickness of 1000Å by DC magnetron sputtering using a Balzers sputtering apparatus. The sputtering conditions at this time were set as 5kW sputtering power and 5 mTorr sputter gas pressure. When observing the crystallized state of the silver reflecting layer at this time using a transmission electron microscope (TEM), the crystal particle sizes were distributed over a range of 200 to 600Å and the average crystal particle size was 510Å.

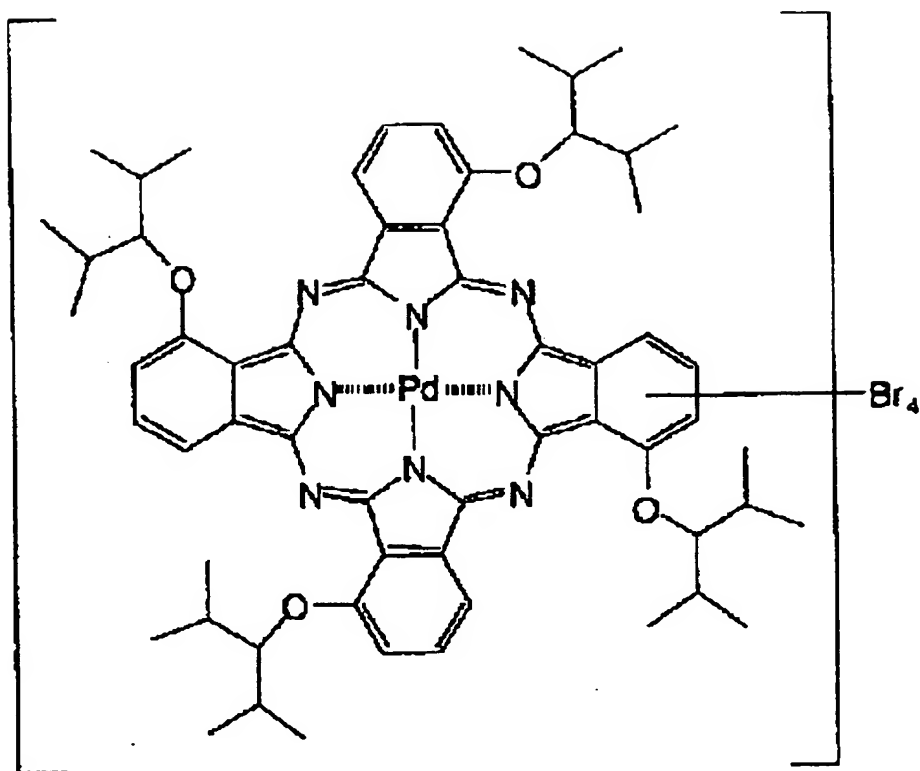
[0029] Furthermore, the reflecting layer was spin coated with the UV curing resin SD-17 (made by Dainippon Ink and Chemicals), then irradiated with UV rays to form a protective layer of a thickness of 6 µm. The thus prepared sample was recorded with an EFM signal using a commercially available CD writer (Philips CDD521). After recording, the error ate was measured using a Pulstec Industrial optical disk evaluation apparatus DDU-1000 and Kenwood CD decoder made (DR-3553).

[0030] This sampel was subjected to a 80°C 85%RH humidity and heat test using a program thermohygrostat (HIFLEX-FX2200 made by ETAC) and the error rates (BLER) after 500, 1000, and 2000 hours were measured.

[0031]

[Formula 1]

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[0032] [Comparative Example 1] Except for changing the sputter power to 0.5 kW, the same procedure was followed as in Example 1 to produce an optical recording medium. When observing the silver reflecting layer at this time by a TEM, the crystal particle sizes were distributed in a range of 700 to 1000Å and the average crystal particle size was 920Å. This medium was recorded with an EFM signal using a commercial CD writer in the same way as in Example 1 to measure the error rate. Moreover, an 80°C 85%RH humidity and heat resistance test was performed in the same way as in Example 1.

[0033] [Example 2] Except for using silver which contains 3 atm% of indium as an impurity, the same procedure was used as in Example 1 to produce an optical recording medium. When the silver reflecting layer at this time was observed by a TEM, the crystal particle sizes were distributed over a range of 100 to 500Å and the average crystal particle size was 390Å. This medium was recorded with an EFM signal using a commercial CD writer in the same way as in Example 1 to measure the error rate. Moreover, an 80°C 85%RH humidity and heat resistance test was performed in the same way as in Example 1.

[0034] [Comparative Example 2] Except for making the sputter power 1 kW and the thickness of the silver reflecting layer 2000Å, the same procedure was followed as in Example 1 to produce an optical recording medium. When observing the silver reflecting layer at this time by a TEM, the crystal particle sizes were distributed in a range of 1200 to 1600Å and the average crystal particle size was 1460Å. This medium was recorded with an EFM signal using a commercial CD writer in the same way as in Example 1 to measure the error rate. Moreover, an 80°C 85%RH humidity and heat resistance test was performed in the same way as in Example 1. The results are summarized in Table 1.

[0035]

[Table 1]

	Average crystal particle size	80°C 85% RH humidity and heat resistance test BLER (c/s)			
		0 hr	500 hrs	1000 hrs	2000 hrs
Ex. 1	510Å	<5	<5	<5	<5
Comp. Ex. 1	920Å	<5	480	1370	7450
Ex. 2	390Å	<5	<5	<5	<5
Comp. Ex. 2	1460Å	<5	990	4530	7450

[0036]

[Effect of the Invention] According to the present invention, by making the average crystal particle size of the silver reflecting layer within the range of 200 to 600Å, it is possible to provide an optical recording medium which has excellent durability and good recording/ reproducing characteristics.

## [BRIEF DESCRIPTION OF THE DRAWINGS]

[FIG. 1] Cross-sectional view of the layer configuration of an optical recording medium

## [Description of Notations]

- 1 Substrate
- 2 Recording layer
- 3 Light reflecting layer
- 4 Protective layer